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SOME EXPERIMENTAL DATA ON THE HEATS OF COMBUSTION OF BENZOIC ACID AND CARBON (GRAPHITE)

By Edward J. Prosen and Frederick D. Rossini

ABSTRACT

Some experimental data are reported on the heats of combustion of benzoic acid and carbon (graphite). The data on benzoic acid support the change in the value for its heat of combustion recently reported from this Bureau by Jessup. The data on carbon (graphite) yield a slightly higher value for the heat of formation of carbon dioxide than that previously reported.

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I. INTRODUCTION

This paper presents some experimental data on the heats of combustion of benzoic acid and of carbon (graphite). The data on benzoic acid have already been referred to by Jessup [6]¹ in his report on the new value for its heat of combustion. The data on carbon (graphite) are being utilized in the selection of a new best value for the heat of formation of carbon dioxide [9].

¹ Figures in brackets indicate the literature references at the end of the paper.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the international joule determined by the standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau [1].

The atomic weights of oxygen, hydrogen, and carbon were taken as 16.0000, 1.0080, and 12.010, respectively, from the 1941 table of International Atomic Weights [2].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [3].

Definitions of the symbols used are given in previous papers [4, 5].

III. METHOD

The method used in the present investigation is described in the report on the heats of combustion of the normal paraffin hydrocarbons [5].

IV. CHEMICAL APPARATUS, MATERIALS, AND PROCEDURE

1. SOURCE AND PURITY OF THE MATERIALS

The benzoic acid used in the combustion experiments of series I, II, III, IV, and V was NBS Standard Sample 39 e. The benzoic acid used in the experiments on calorimeter system *D* was NBS Standard Sample 39 f. These samples have been described previously by Jessup [6].

The samples of artificial graphite and Buckingham natural graphite were from the same source as those measured by Jessup [10]. The artificial graphite was of "spectrographic" grade² and was reported by the maker (National Carbon Co.) to contain less than 0.001 percent of ash. The Buckingham natural graphite was purified by alternate treatments with hydrochloric acid and hydrofluoric acid by H. B. Knowles, of this Bureau. The effect of various purification treatments has been reported by Jessup [10].

2. PREPARATION OF THE SAMPLES FOR COMBUSTION

The benzoic acid (about 1.51 g per experiment) was tightly pressed into a cylindrical pellet one-half inch in diameter in a pellet press. The benzoic acid was weighed in the platinum crucible (mass 8.2 g) in which it was burned.

The artificial graphite was burned in the form of a powder and the Buckingham natural graphite in the form of fine flakes. In each case, a sample of about 1.23 g was placed in a pile in the platinum crucible (mass 8.2 g), or in one of two platinum dishes (mass 1.6 g or 0.7 g) in which it was burned.

² See the spectrochemical analysis of another sample of this material reported by B. F. Scribner, of this Bureau, in table 5 of reference [10].

3. IGNITION OF THE SAMPLES

The samples were ignited in the bomb by a coil of 5 cm of Parr wire placed about 1 mm above the sample in the platinum crucible or dish [4].

4. PURIFICATION OF THE OXYGEN

The oxygen for combustion was purified as described previously [4].

5. EXAMINATION OF THE PRODUCTS OF COMBUSTION

The products of combustion were examined as previously described [4]. No products of incomplete combustion were detected in the gaseous products from any of the experiments with benzoic acid or with graphite. In the experiments with graphite, a small amount (several milligrams) of the sample remained unburned.

6. DETERMINATION OF THE AMOUNT OF REACTION

For the combustion experiments on graphite, the amount of reaction was determined from the mass of carbon dioxide formed, with 44.010 g of carbon dioxide being taken as equivalent to 1 mole of carbon.

For the experiments on benzoic acid, the amount of reaction was determined from the mass of benzoic acid placed in the bomb, for the purpose of better comparison with the results of Jessup [6]. In addition, as a further check on the purity of the chemical reaction occurring in the combustion experiment, measurements of the carbon dioxide formed in the combustion in the bomb were made in two series of experiments with benzoic acid. The results of these measurements, giving the ratio of the mass of carbon dioxide formed to the amount of carbon dioxide calculated stoichiometrically from the mass of sample, are as follows:

Series	Number of experiments	Average ratio	Standard deviation of the mean
(1)-----	6	0.999954	± 0.000080
(2)-----	4	.999987	$\pm .000081$

V. CALORIMETRIC APPARATUS AND PROCEDURE

1. APPARATUS

The apparatus used in this work was the same as that described in references [4] and [5]. The calorimeter systems *A*, *B*, and *C* referred to in this report are identical with those described in reference [5]. For the later experiments on graphite, calorimeter system *D* was used, which differed from calorimeter system *C* only in the calorimeter heater. The latter consisted of a heating element of about 150 ohms of manganin wire (No. 30 AWG) spiraled inside a copper tube one-quarter inch in diameter and 6 feet long, with magnesia insulation. This heater turned out to be unsatisfactory for use in precise experiments with electric energy because the electrical insulation was not good enough, and it was therefore used only to bring the calorimeter

system to the proper starting temperature. On this account, the energy equivalent of calorimeter system *D* had to be determined in terms of that of calorimeter system *C* by the use of benzoic acid to obtain the ratio of the two energy equivalents.

2. DETERMINATION OF THE IGNITION ENERGY

The ignition energy was determined as described in reference [4].

3. CORRECTION FOR THE FORMATION OF NITRIC ACID

The correction for the nitric acid formed in the reaction in the bomb was made as described previously [4, 5].

4. ELECTRIC-ENERGY EQUIVALENT

The experiments made to determine the electric-energy equivalent of calorimeter systems *A*, *B*, and *C* are described in detail in reference [5]. The energy equivalent of calorimeter system *D* was determined in terms of that of calorimeter system *C* by the use of benzoic acid (NBS Standard Sample 39 e with calorimeter system *C* and NBS Standard Sample 39 f with calorimeter system *D*) to obtain the ratio of the two energy equivalents. These two samples of purified benzoic acid were essentially identical in purity, and Jessup found no significant difference in their heats of combustion [6].

5. COMBUSTION EXPERIMENTS

The procedure followed in performing the calorimetric combustion experiments is described in detail on pages 302 and 303 of reference [4].

VI. RESULTS OF THE PRESENT INVESTIGATION

1. ELECTRIC-ENERGY EQUIVALENT

The electric-energy equivalents of calorimeter systems *A*, *B*, and *C* are given in reference [5]. The results of the experiments to determine the energy equivalent of calorimeter system *D* through its ratio to that of calorimeter system *C*, by the use of benzoic acid, are given in table 1. For convenience and clarity in presentation, the data are all reported in terms of the energy equivalent of calorimeter system *C*, and the following relations were used for the ratios of the energy equivalents of the several systems:

$$E_s(C) = 137717.4 \pm 13.9 \text{ int. j/ohm.}$$

$$E_s(A) = 0.998955 E_s(C) = 137573.5 \pm 16.2 \text{ int. j/ohm.}$$

$$E_s(B) = 1.002003 E_s(C) = 137993.3 \pm 14.6 \text{ int. j/ohm.}$$

$$E_s(D) = 0.991085 E_s(C) = 136489.6 \pm 14.5 \text{ int. j/ohm.}$$

TABLE 1.—Energy equivalent of calorimeter system D

Experiment number	Mass of benzoic acid ^a	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_c	Δr_i	Δr_n	<i>B'</i>	Deviation from mean
	<i>g</i>	<i>min</i> ⁻¹	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm/g of benzoic acid</i>	<i>Ohm/g of benzoic acid</i>
1.....	1.51973	0.002005	0.000934	0.000474	0.294674	0.000409	0.000045	0.1936238	0.0000091
2.....	1.52023	.001973	0.00860	.000446	.294770	.000416	.000051	.1936147	.0000000
3.....	1.50071	.001967	.001014	.000480	.290981	.000418	.000047	.1936084	-.0000063
4.....	1.53028	.001972	.000856	.000432	.296711	.000414	.000053	.1936119	-.0000028
Mean								0.1936147	
Standard deviation of the mean								±.0000033	

^a NBS Standard Sample 39f.

2. COMBUSTION EXPERIMENTS

The results of five series of experiments on the combustion of benzoic acid are given in table 2, in which the symbols have the same meaning as before [4, 5], except that *B'* is the corrected rise in temperature of the standard calorimeter system, expressed in ohms on the given platinum resistance thermometer, divided by the mass of benzoic acid.

TABLE 2.—Combustion experiments on benzoic acid

Series number	Number of experiments ^a			Mass of benzoic acid ^b	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_c	Δr_i	Δr_n	<i>B'</i>	
	<i>A</i>	<i>B</i>	<i>C</i>								Mean	Standard deviation of mean
				<i>g</i>	<i>min</i> ⁻¹	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm/g benzoic acid</i>	<i>Ohm/g benzoic acid</i>
I.....	5			{1.51447 to 1.51505 1.50186	{0.001927 to .001937 .001940	{0.000993 to .001040 .001060	{0.000098 to .000114 .000074	{0.291335 to .291476 .288031	{0.000406 to .000426 .000408	{0.000023 to .000027 .000063	{0.1918961 to .1919072	{±0.0000088 to ±.0000157
II.....		6		{1.51581 to 1.51470	{0.001951 to .001934	{0.001151 to .000782	{0.000125 to .000530	{.290703 to .290615	{0.000420 to .000393	{0.000072 to .000064	{.1918792 to .1918792	{±.0000215 to ±.0000215
III.....		4		{1.51800 to 1.51796	{0.001946 to .001928	{0.001224 to .000806	{0.000565 to .000179	{.291283 to .291165	{0.000414 to .000409	{0.000076 to .000074	{.1918608 to .1918608	{±.0000190 to ±.0000190
IV.....		4		{1.51873 to 1.49749	{0.001938 to .001944	{0.001244 to .001224	{0.000195 to .000275	{.291391 to .287718	{0.000415 to .000403	{0.000079 to .000013	{.1918857 to .1918857	{±.0000109 to ±.0000109
V.....			5	{1.52035	{0.001954	{0.001345	{0.000349	{.292072	{0.000418	{0.000013	{.1918886	{±.0000109 to ±.0000109
Weighted mean											0.1918886	

^a The numbers in columns *A*, *B*, and *C* indicate the number of experiments performed with calorimeter systems *A*, *B*, *C*, respectively (see section V-1).^b NBS Standard Sample 39 e.

The results of the four series of experiments on the combustion of Buckingham natural graphite and artificial graphite are given in table 3.

TABLE 3.—Combustion experiments on graphite

Substance	Series number	Number of experiments ^a		Mass of carbon dioxide formed	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_e	Δr_i	Δr_n	<i>B</i>	
		<i>C</i>	<i>D</i>								Mean	Standard deviation of mean
Buckingham natural graphite.....	<div><div>I</div><div>II</div></div>	5	4	<div><div><i>g</i></div><div>4.50052</div><div>to</div><div>4.53686</div><div>4.30513</div><div>to</div><div>4.58939</div></div> <div><div><i>min</i>⁻¹</div><div>0.001942</div><div>to</div><div>.001958</div><div>.002017</div><div>to</div><div>.001970</div></div> <div><div><i>Ohm</i></div><div>0.001273</div><div>to</div><div>.001428</div><div>.000449</div><div>to</div><div>.001072</div></div> <div><div></div><div>0.000300</div><div>to</div><div>.000342</div><div>.000430</div><div>to</div><div>.000474</div></div> <div><div></div><div>0.292856</div><div>to</div><div>.295272</div><div>.282664</div><div>to</div><div>.301402</div></div> <div><div></div><div>0.000379</div><div>to</div><div>.000409</div><div>.000393</div><div>to</div><div>.000416</div></div> <div><div></div><div>0.000002</div><div>to</div><div>.000002</div><div>.000008</div><div>to</div><div>.000013</div></div>	<div><div><i>Ohm/g CO₂</i></div><div>0.0649887</div></div> <div><div><i>Ohm/g CO₂</i></div><div>±0.0000029</div></div> <div><div></div><div>.0649927</div></div> <div><div></div><div>±.0000076</div></div>							
Artificial graphite.....	<div><div>I</div><div>II</div></div>	5	3	<div><div>4.50375</div><div>to</div><div>4.52566</div><div>4.49369</div><div>to</div><div>4.51621</div></div> <div><div>to</div><div>to</div><div>.001962</div><div>.001976</div><div>to</div><div>.001988</div></div> <div><div></div><div>.001042</div><div>to</div><div>.001315</div><div>.000724</div><div>to</div><div>.001071</div></div> <div><div></div><div>.000308</div><div>to</div><div>.000376</div><div>.000378</div><div>to</div><div>.000456</div></div> <div><div></div><div>.293214</div><div>to</div><div>.294588</div><div>.295225</div><div>to</div><div>.296666</div></div> <div><div></div><div>.000405</div><div>to</div><div>.000417</div><div>.000409</div><div>to</div><div>.000419</div></div> <div><div></div><div>.000002</div><div>to</div><div>.000003</div><div>.000024</div><div>to</div><div>.000041</div></div>	<div><div><i>Ohm/g CO₂</i></div><div>0.0649972</div></div> <div><div><i>Ohm/g CO₂</i></div><div>±.0000050</div></div> <div><div></div><div>.0649997</div></div> <div><div></div><div>±.0000124</div></div>							
Weighted mean.....											0.0649920	-----

^a The numbers in columns *C* and *D* indicate the number of experiments performed with calorimeter systems *C* and *D*, respectively (see section V-1).

As stated in the preceding section, all the foregoing values of B and B' are expressed in terms of the energy equivalent of system C .

3. VALUES OF THE HEATS OF COMBUSTION

The value of the heat evolved in the combustion of benzoic acid under the conditions of the bomb process, for 28° C, is the product of the mean value of B' (from table 2) and of $E_s(C)$, the energy equivalent of calorimeter system C :

$$Q'_B(28^\circ \text{ C}) = 26426.4 \pm 2.2 \text{ int. j/g.}$$

Conversion to 25° C, and the standard conditions of the bomb process [11], by the use of the relation given in footnote 6, page 261, of reference [6], yields

$$Q_B(25^\circ \text{ C}) = 26429.3 \pm 2.2 \text{ int. j/g.}$$

The value of the heat of combustion of graphite in the bomb process is the product of the mean value of B (table 3), the energy equivalent of calorimeter system C , and the molecular weight of carbon dioxide [5]:

$$-\Delta U_B(28^\circ \text{ C}) = 393913 \pm 55 \text{ int. j/mole.}$$

Conversion to $-\Delta Hc^\circ$ at 25° C, which is the decrement in heat content with both reactants and the product in their thermo-dynamic reference states, yields

$$-\Delta Hc^\circ (25^\circ \text{ C}) = 393502 \pm 55 \text{ int. j/mole.}$$

The conversion to $-\Delta Hc^\circ$ at 25° C involves -409 j/mole in the Washburn correction [11], $+1$ j/mole for $P\Delta V$, and -3 j/mole for the change from 28° to 25° C.

The over-all uncertainty assigned to each final value above was taken as the square root of the sum of the squares of the following components, as appropriate: (a) Twice the standard deviation of the mean of the series of combustion experiments; (b) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of reaction; (c) twice the standard deviation of the mean (or weighted mean) of the series of experiments to determine the energy equivalent; and (d) an uncertainty of 0.010 percent in the determination of the absolute value of the electric energy.

VII. DISCUSSION

The value for the heat of combustion of benzoic acid obtained in this investigation is in complete accord with that reported recently from this Bureau by Jessup [6], the difference being 0.003 ± 0.013 percent.

The value for the heat of combustion of graphite given here is slightly higher than that previously reported, and the data are being used in another report [9], in conjunction with a recalculation of the data previously reported [10, 12, 13], to obtain a selected "best" value for the heat of formation of carbon dioxide.

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